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(54)【発明の名称】　ポリオレフィン微多孔膜

(57)【要約】

【課題】　透過性能及び機械的強度に優れるとともに、成形時の曲がり等が少なく、電解液の保持量の優れたポリオレフィン微多孔膜を提供する。

【解決手段】　重量平均分子量が５×１０⁵以上のポリエチレンまたはそのポリエチレン組成物７０～９５重量％と、重量平均分子量が１×１０⁴以上のポリプロピレン５～３０重量％を含有するポリオレフィン組成物からなるポリオレフィン微多孔膜であって、膜表面の面方向に隣り合う左右四方１mm以内の厚み変動が±１μm以上にし、ポリオレフィン微多孔膜の表面に微視的な凹凸を生じさせ、成形性、電解液の浸透性、保持性を改良したポリオレフィン微多孔膜。

【特許請求の範囲】

【請求項１】　重量平均分子量が５×１０^{5}以上のポリエチレンまたはそのポリエチレン組成物７０～９５重量％と、重量平均分子量が１×１０^{4}以上のポリプロピレン５～３０重量％を含有するポリオレフィン組成物からなるポリオレフィン微多孔膜であって、膜表面の面方向に隣り合う左右四方１ｍｍ以内の厚み変動が±１μｍ以上であるポリオレフィン微多孔膜。

【請求項２】　請求項１に記載のポリオレフィン微多孔膜からなる電池用セパレーター。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、ポリオレフィン微多孔膜に関するものであって、より詳しくは電池用セパレータ等に使用される、透過性能及び機械的強度に優れるとともに、電解液の浸透性、保持性の優れた機能を有するポリオレフィン微多孔膜に関するものである。

【０００２】

【従来の技術】ポリオレフィン微多孔膜は、有機溶媒に不溶であり、かつ電解質や電極活物質に対して安定であるため、電池のセパレーター、特にリチウムイオン１次・２次電池のセパレーター、電気自動車等の大型電池用セパレーターコンデンサーのセパレーター、各種の分離膜、水処理膜、限外濾過膜、精密濾過膜またははその基材として広く用いられている。

【０００３】最近開発されてきている超高分子量のポリオレフィンを用いた高強度および高弾性のポリオレフィン微多孔膜は、電気抵抗が小さく、薄く、機械強度に優れており、リチウム電池用セパレーターとして用いられている。それらの製造方法としては、例えば、重量平均分子量が７×１０^{5}以上の超高分子量ポリオレフィンを溶媒中で加熱溶解した溶液からゲル状シートを成形し、前記ゲル状シート中の溶媒を脱溶媒処理し、次いで加熱延伸した後、残留溶媒を除去することにより、微多孔膜を製造する方法が提案されている（特開平３－１０５８５１号公報）。

【０００４】上記方法によるポリオレフィン微多孔膜は、延伸条件等によっては、残留歪みによって経時的に変形が起こり、通常使用されている形状である巻物とした時に曲がりや波打ちが発生し易く、電池用セパレーターとして電池に巻き込んだ時に、折れたり蛇行して電極が露出したりして好ましくないという問題があった。さらに、このポリオレフィン微多孔膜を電池用セパレーターとして用いると、孔径が微細であり、かつ電極との接触性が良すぎるために、電池組立工程で電解液の注入量が比較的少なく、電気自動車用の電池に代表される高容量で大型の電池用セパレーターとしては、問題があった。

【０００５】

【発明が解決しようとする課題】したがって、本発明の目的は、透過性能及び機械的強度に優れるとともに、成形時の曲がり等が少なく、電解液の保持量の優れたポリオレフィン微多孔膜を提供することである。

【０００６】

【課題を解決するための手段】本発明者らは、上記目的を達成するため鋭意研究を行った結果、超高分子量ポリエチレンまたはその組成物に特定量のポリプロピレンを加えることにより、ポリオレフィン微多孔膜の表面に微視的な凹凸を生じさせ、透過性能及び機械的強度に優れるとともに、成形性を改善し、電解液の浸透性、保持性を改良したポリオレフィン微多孔膜が得られることを見出し、本発明に想到した。すなわち、本発明は、重量平均分子量が５×１０^{5}以上のポリエチレンまたはそのポリエチレン組成物７０～９５重量％と、重量平均分子量が１×１０^{4}以上のポリプロピレン５～３０重量％を含有するポリオレフィン組成物からなるポリオレフィン微多孔膜であって、膜表面の面方向に隣り合う左右四方１ｍｍ以内の厚み変動が±１μｍ以上であるポリオレフィン微多孔膜である。

【０００７】

【発明の実施の形態】本発明で用いるポリエチレンは、重量平均分子量が５×１０^{5}以上、好ましくは１×１０^6～１５×１０^{6}の超高分子量のポリエチレンである。重量平均分子量が５×１０^{5}未満では、微多孔膜の製造時の延伸工程において最大延伸倍率が低く、目的の微多孔膜が得られない。一方、上限は特に限定的ではないが１５×１０^{6}を超えるものは、微多孔膜の製造時のゲル状成形物の形成において成形性に劣る。また、本発明においては、後述のポリオレフィン溶液の高濃度化と微多孔膜の強度の向上を図るために、重量平均分子量１×１０^{6}以上の超高分子量ポリエチレンと重量平均分子量１×１０^{5}以上５×１０^{5}未満の高密度ポリエチレンとの組成物を用いることができる。超高分子量ポリエチレンのポリエチレン組成物中の含有量は、ポリエチレン組成物全体を１００重量％として１重量％以上が好ましく、より好ましくは１０～７０重量％である。さらに前記ポリエチレンまたはそのポリエチレン組成物の分子量分布の尺度として用いられる重量平均分子量／数平均分子量は３００以下、好ましくは５～５０である。

【０００８】本発明で用いるポリプロピレンとしては、重量平均分子量が１．０×１０^{4}以上、好ましくは３．０×１０^4～１．０×１０^{6}のホモポリプロピレン、エチレン含有量が１．０重量％以下のエチレンプロピレンランダムコポリマー、エチレンプロピレンブロックコポリマー等を用いることができる。重量平均分子量が１．０×１０^{4}未満では、得られるポリオレフィン微多孔膜の開孔が困難になり、エチレン含有量が１．０重量％を超えるとポリオレフィンの結晶性が低くなり、ポリオレフィン微多孔膜の開孔が困難になる。

【０００９】ポリプロピレンをポリエチレンまたはその

ポリエチレン組成物に加えることにより、得られたポリオレフィン微多孔膜の表面に微視的凹凸が生じる。この微視的凹凸は、ポリオレフィン膜表面の面方向に隣り合う左右四方１ｍｍ以内の厚み変動が±１μｍ以上、好ましくは±１μｍ～±３μｍである。厚み変動が±１μｍ未満では、電解液の保持性の向上には効果がない。本発明で用いるポリプロピレンの量は、ポリオレフィン全体の５～３０重量％、好ましくは、５～２５重量％である。５重量％未満では、均一に多数分散した凹凸を形成できず、電解液保持性向上の効果はみられない。また、３０重量％を超えるとポリオレフィン微多孔膜の強度が著しく低下し、さらに多くなるとシート成形時にポリエチレンとポリプロピレンが相分離してしまい、成形が困難になる。

【００１０】本発明のポリオレフィン微多孔膜は、ポリエチレンまたはポリエチレン組成物にポリプロピレンを加えた樹脂組成物に有機液状体または固体を混合し、溶融混練後押出成形し、抽出、延伸を施すことにより得られる。また、樹脂組成物および有機液状体または固体の混合物に無機微粉体を添加しても何等差し支えない。本発明のポリオレフィン微多孔膜を得る好ましい方法としては、ポリオレフィン組成物にポリオレフィンの良溶媒を供給しポリオレフィン組成物の溶液を調製して、この溶液を押出機のダイよりシート状に押し出した後、冷却してゲル状組成物を形成して、このゲル状組成物を加熱延伸し、しかる後残存する溶媒を除去する方法である。

【００１１】本発明において、原料となるポリオレフィン組成物の溶液は、上述のポリオレフィン組成物を、溶媒に加熱溶解することにより調製する。この溶媒としては、ポリオレフィンを十分に溶解できるものであれば特に限定されない。例えば、ノナン、デカン、ウンデカン、ドデカン、流動パラフィンなどの脂肪族または環式の炭化水素、あるいは沸点がこれらに対応する鉱油留分などがあげられるが、溶媒含有量が安定なゲル状成形物を得るためには流動パラフィンのような不揮発性の溶媒が好ましい。加熱溶解は、ポリオレフィンが完全に溶解する温度で強力に撹拌または押出機で混練しながら行う。その温度は、例えば１４０～２５０℃の範囲が好ましい。またポリオレフィン溶液の濃度は、１０～５０重量％好ましくは１０～４０重量％である。濃度が１０重量％未満では、使用する溶媒量が多く経済的でないばかりか、シート状に成形する際に、ダイス出口でスウェルやネックインが大きくシートの成形が困難となる。なお、加熱溶解にあたってはポリオレフィンの酸化を防止するために酸化防止剤を添加するのが好ましい。

【００１２】次にこのポリオレフィン組成物の加熱溶液を好ましくはダイから押し出して成形する。ダイは、通常長方形の口金形状をしたシートダイが用いられるが、２重円筒状のインフレーションダイなども用いることができる。シートダイを用いた場合のダイギャップは通常０．１～５ｍｍであり、押し出し成形温度は１４０～２５０℃である。この際押し出し速度は、通常２０～３０ｃｍ/分ないし１０ｍ/分である。

【００１３】このようにしてダイから押し出された溶液は、冷却することによりゲル状シートに成形される。冷却は少なくともゲル化温度以下までは５０℃／分以上の速度で行うのが好ましい。一般に冷却速度が遅いと、得られるゲル状シートの高次構造が粗くなり、それを形成する疑似細胞単位も大きなものとなるが、冷却速度が速いと、密な細胞単位となる。冷却速度が５０℃／分未満では、結晶化度が上昇し、延伸に適したゲル状シートとなりにくい。冷却方法としては、冷風、冷却水、その他の冷却媒体に直接接触させる方法、冷媒で冷却したロールに接触させる方法などを用いることができる。なお、ダイから押し出された溶液は、冷却前あるいは冷却中に好ましくは１～１０、より好ましくは１～５の引き取り比で引取ってもよい。引き取り比が１０以上になるとネックインが大きくなり、また延伸時に破断を起こしやすくなり好ましくない。

【００１４】次に、このゲル状成形物に延伸を行う。延伸はゲル状シートを加熱し、通常のテンター法、ロール法、インフレーション法、圧延法もしくはこれらの方法の組み合わせによって所定の倍率で行う。延伸は一軸延伸でも二軸延伸でもよいが、二軸延伸が好ましい。また、二軸延伸の場合は、縦横同時延伸または逐次延伸のいずれでもよい。延伸温度はポリオレフィンの融点＋１０℃以下、好ましくはポリオレフィンの結晶分散温度から結晶融点未満の範囲である。また延伸倍率は原反の厚さによって異なるが、一軸延伸では２倍以上が好ましく、より好ましくは３～３０倍である。二軸延伸では面倍率で１０倍以上が好ましく、より好ましくは１５～４００倍である。面倍率が１０倍未満では延伸が不十分で高弾性、高強度の微多孔膜が得られない。一方、面倍率が４００倍を超えると、延伸操作などで制約が生じる。

【００１５】得られた延伸成形物は、溶剤で洗浄し残留する溶媒を除去する。洗浄溶剤としては、ペンタン、ヘキサン、ヘプタンなどの炭化水素、塩化メチレン、四塩炭素などの塩素化炭化水素、三フッ化エタンなどのフッ化炭化水素、ジエチルエーテル、ジオキサンなどのエーテル類などの易揮発性のものを用いることができる。これらの溶剤はポリオレフィン組成物の溶解に用いた溶媒に応じて適宜選択し、単独もしくは混合して用いる。洗浄方法は、溶剤に浸漬し抽出する方法、溶剤をシャワーする方法、またはこれらの組合せによる方法などにより行うことができる。

【００１６】上述のような洗浄は、延伸成形物中の残留溶媒が１重量％未満になるまで行う。その後洗浄溶剤を乾燥するが、洗浄溶剤の乾燥方法は加熱乾燥、風乾などの方法で行うことができる。乾燥した延伸成形物は、結晶分散温度～融点の温度範囲で熱固定することが望まし

い。

【００１７】以上のようにして製造したポリオレフィン微多孔膜は、巻スリットにした時の曲がりが小さく、電解液の保持量が多く、電池用セパレーターとして用いると、その容量を高くすることができる。なお、得られたポリオレフィン微多孔膜は、必要に応じてさらに、プラズマ照射、界面活性剤含浸、表面グラフト等の親水化処理などの表面修飾を施すことができる。

【００１８】

【実施例】以下に本発明について実施例を挙げてさらに詳細に説明するが、本発明は実施例に特に限定されるものではない。なお、実施例における試験方法は次の通りである。

（１）膜厚：断面を走査型電子顕微鏡により測定した。

（２）厚み変動：アンリツ（株）製フィルムシックネステスタＫＧ６０１Ａでポリオレフィン微多孔膜の厚み分布を０．１μｍの高分解能で連続測定し、厚み分布を測定した。

（３）破断強度：幅１５ｍｍ短冊状試験片の破断強度をＡＳＴＭ　Ｄ８８２に準拠して測定した。

（４）透気度：ＪＩＳ　Ｐ８１１７に準拠して測定した。

（５）曲がり：６０mm幅、５００m巻きにスリットした巻物を１m巻き出した時の曲がりを測定した。

（６）電解液量：１０ｃｍ×１０ｃｍのサンプルを１０枚重ね、５ｋｇの圧力で圧縮しながら、サイドから電解液（プロピレンカーボネイト）を注入して、微多孔膜に注入できる電解液量を測定した。

【００１９】実施例１

重量平均分子量が２．５×１０^{6}の超高分子量ポリエチレン（ＵＨＭＷＰＥ）２０重量%、３．５×１０^{5}の高密度ポリエチレン（ＨＤＰＥ）６０重量%及び重量平均分子量が５．１×１０^{5}のポリプロピレンが２０重量%からなるポリオレフィン組成物１００重量部に酸化防止剤０．３７５重量部を加えたポリオレフィン組成物を得た。このポリオレフィン組成物３０重量部を二軸押出機（５８mmφ、Ｌ／Ｄ＝４２、強混練タイプ）に投入した。またこの二軸押出機のサイドフィーダーから流動パラフィン７０重量部を供給し、２００ｒｐｍで溶融混練して、押出機中にてポリオレフィン溶液を調製した。

【００２０】続いて、この押出機の先端に設置されたＴダイから１９０℃で押し出し、冷却ロールで引取りながらゲル状シートを成形した。続いてこのゲル状シートを、１１５℃で５×５に同時２軸延伸を行い、延伸膜を得た。得られた延伸膜を塩化メチレンで洗浄して残留する流動パラフィンを抽出除去した後、乾燥および熱処理を行いポリオレフィン微多孔膜を得た。このポリオレフィン微多孔膜の物性評価の結果を表１に示す。

【００２１】実施例２

実施例１において、樹脂組成物と流動パラフィンの使用量を表１に示す値に変更した以外は、実施例１と同様にして微多孔膜を得た。得られたポリオレフィン微多孔膜の物性評価の結果を表１に示す。

【００２２】実施例３

実施例１において、ポリプロピレンの使用量を表１に示す値に変更した以外は、実施例１と同様にして微多孔膜を得た。得られたポリオレフィン微多孔膜の物性評価の結果を表１に示す。

【００２３】実施例４

実施例１において、ポリプロピレンの分子量及び使用量を表１に示す値に変更した以外は、実施例１と同様にして微多孔膜を得た。得られたポリオレフィン微多孔膜の物性評価の結果を表１に示す。

【００２４】比較例１

実施例１において、ポリプロピレンを用いない以外は、実施例１と同様にして微多孔膜を得た。得られたポリオレフィン微多孔膜の物性評価の結果を表１に示す。

【００２５】表１から明らかなように、実施例１～４に例示されている本発明のポリオレフィン微多孔膜は、膜表面に微視的凹凸が生じており、成形時の曲がりが少なく、電解液保持量が多い。一方、ポリプロピレンを添加しない組成物からのポリエチレン微多孔膜は、膜表面に微視的凹凸が無く、成形時の曲がりが大きく、電解液保持量が少ない（比較例１）。

【００２６】

【表１】

7　8

	実施例				比較例
	1	2	3	4	1
ﾎﾟﾘｴﾁﾚﾝ UHMWPE(Mw)　(重量%) HDPE(Mw)　(重量%)	2.5×10^6(20) 3.5×10^5(60)	2.5×10^6(20) 3.5×10^5(70)	2.5×10^6(20) 3.5×10^5(70)	2.5×10^6(20) 3.5×10^5(60)	2.5×10^6(20) 3.3×10^5(60)
ﾎﾟﾘﾌﾟﾛﾋﾟﾚﾝ Mw　(重量%)	5.1×10^5(20)	5.1×10^5(10)	5.1×10^5(10)	1.5×10^5(20)	－
樹脂濃度(重量%)	30	40	30	30	30
流動ﾊﾟﾗﾌｨﾝ(重量%)	70	60	70	70	70
延伸条件 温度（℃） 倍率	 115 5×5	 115 5×5	 115 5×5	 115 5×5	 115 5×5
膜物性 膜厚(μm) 厚み変動（μm） 破断強度 MD/TD (kg/cm^2) 透気度(秒/100cc) 曲がり（mm） 電解液量（g）	 25.5 1.35 1100/950 550 1 0.95	 26 1.10 1210/1010 690 1.5 0.73	 26.8 1.20 1160/990 705 2.2 0.84	 26.8 1.15 965/830 662 2.2 0.79	 25 0.49 1250/1130 730 8 0.4

【００２７】

【発明の効果】本発明のポリオレフィン微多孔膜は、成形時の曲がりが小さく、電解液保持量が多く、高強度、高透過性でであることから安全性が高く、高容量リチウム電池用セパレーターとして用いる場合は安全性の点でおおいに信頼できる。

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(21)Application number : 10-090686 (71)Applicant : TONEN KAGAKU KK

(22)Date of filing : 20.03.1998 (72)Inventor : TAKITA KOTARO

FUNAOKA HIDEHIKO

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KONO KOICHI

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(54) POLYOELFIN FINE POROUS MEMBRANE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide polyolefin fine porous membranes excellent in permeation performance and mechanical strengths, reduced in bends or the like at the time of molding and excellent in retention volume of an electrolyte.

SOLUTION: A desired polyolefin fine porous membrane is made of a polyolefin composition comprising 70-95 wt.% polyethylene having a weight average molecular weight of 5×105 or more or polyethylene composition thereof and 5-30 wt.% polypropylene having a weight average molecular weight of 1×104 or more. In this instance, the thickness variation within an adjoining area of 1 mm2 in every area direction in the surface of the membrane is rendered ±1 μm or more

to cause microscopic recesses and projections on the surface of the polyolefin fine porous membrane and as a result, the moldability, the permeability and retention of an electrolyte are improved.

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* NOTICES *

CLAIMS

[Claim(s)]

[Claim 1] Polyolefine fine porosity film whose thickness fluctuation of less than 1mm of right-and-left four way types with which weight average molecular weight is the polyolefine fine porosity film which consists of 5x105 or more polyethylene or 70 - 95 % of the weight of a polyethylene constituent of those, and a polyolefine constituent with which weight average molecular weight contains 5 - 30 % of the weight of 1x104 or more polypropylene, and adjoins each other in the direction of a field on the front face of the film is **1 micrometers or more.

[Claim 2] The separator for cells which consists of polyolefine fine porosity film according to claim 1.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polyolefine fine porosity film which has the function which was excellent in the permeability of the electrolytic solution, and holdout while it is excellent in the penetrable ability and the mechanical strength which are used for the separator for cells etc. in more detail about the polyolefine fine porosity film.

[0002]

[Description of the Prior Art] The polyolefine fine porosity film is insoluble to an organic solvent, and to the electrolyte or the electrode active material, since it is stable, it is widely used as the separator of separator capacitors for large-sized cells, such as a separator of a cell especially a separator of the primary lithium ion and a rechargeable battery, and an electric vehicle, various kinds of demarcation membranes, the water treatment film, ultrafiltration membrane, a micro filter, or a base material of ****.

[0003] The polyolefine fine porosity film of the high intensity and high elasticity using the polyolefine of ultrahigh molecular weight developed recently has small electric resistance, is thin, is excellent in mechanical strength, and is used as a

separator for lithium cells. After weight average molecular weight fabricates a gel sheet from the solution which carried out the heating dissolution of the 7x105 or more ultrahigh-molecular-weight polyolefines in the solvent, carries out deliquoring processing of the solvent in said gel sheet and subsequently carries out heating extension as those manufacture approaches, for example, the method of manufacturing the fine porosity film is proposed by removing a residual solvent (JP,3-105851,A).

[0004] When it considered as the roll which is the configuration usually used, it was easy to generate deflection and flapping, and deformation took place with time by residual distortion, the electrode was [when it involved in a cell as a separator for cells, it broke, or] meanderingly exposed with extension conditions etc., and the polyolefine fine porosity film by the above-mentioned approach had the problem of not being desirable. Furthermore, when this polyolefine fine porosity film was used as a separator for cells, since an aperture was detailed and contact nature with an electrode was too good, there were comparatively few injection rates of the electrolytic solution as a cell erector, and there was a problem as a separator for cells large-sized at the high capacity represented by the cell for electric vehicles.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, there is little deflection at

the time of shaping etc., and the purpose of this invention is offering the polyolefine fine porosity film which was excellent in the amount of maintenance of the electrolytic solution while it is excellent in penetrable ability and a mechanical strength.

[0006]

[Means for Solving the Problem] this invention persons have improved the moldability and hit on an idea of the polyolefine fine porosity film which improved the permeability of the electrolytic solution and holdout being obtained to a header and this invention while they made the front face of the polyolefine fine porosity film produce microscopic irregularity and were excellent in penetrable ability and a mechanical strength by adding the polypropylene of the amount of specification to ultra high molecular weight polyethylene or its constituent, as a result of inquiring wholeheartedly, in order to attain the above-mentioned purpose. That is, this invention is polyolefine fine porosity film whose thickness fluctuation of less than 1mm of right-and-left four way types with which weight average molecular weight is the polyolefine fine porosity film which consists of 5x105 or more polyethylene or 70 - 95 % of the weight of a polyethylene constituent of those, and a polyolefine constituent with which weight average molecular weight contains 5 - 30 % of the weight of 1x104 or more polypropylene, and adjoins each other in the direction of a field on the front face of the film is **1

micrometers or more.

[0007]

[Embodiment of the Invention] The weight average molecular weight of the polyethylene used by this invention is polyethylene of the ultrahigh molecular weight of 1x106 to 15x106 preferably 5x105 or more. In the extension process at the time of manufacture of the fine porosity film, the maximum draw magnification has low weight average molecular weight at less than 5x105, and the target fine porosity film is not obtained. On the other hand, what exceeds 15x106 although especially an upper limit is not restrictive is inferior to a moldability in formation of the gel moldings at the time of manufacture of the fine porosity film. Moreover, in this invention, in order to aim at improvement in high-concentration-izing of the below-mentioned polyolefine solution, and the reinforcement of the fine porosity film, the constituent of with a weight average molecular weight of 1x106 or more ultra high molecular weight polyethylene, and 1x105 or more weight-average-molecular-weight less than 5x105 high density polyethylene can be used. The content in the polyethylene constituent of ultra high molecular weight polyethylene makes the whole polyethylene constituent 100 % of the weight, and 1 % of the weight or more is desirable, and it is 10 - 70 % of the weight more preferably. The weight average molecular weight/number average molecular weight furthermore used as a scale of the

molecular weight distribution of said polyethylene or its polyethylene constituent are 5-50 preferably 300 or less.

[0008] As polypropylene used by this invention, the gay polypropylene of 3.0x104 to 1.0x106 and an ethylene content can use [weight average molecular weight] 1.0 or less % of the weight of an ethylene propylene random copolymer, an ethylene propylene block copolymer, etc. preferably 1.0x104 or more. Puncturing of the polyolefine fine porosity film with which weight average molecular weight is obtained less than by 1.0x104 becomes difficult, if an ethylene content exceeds 1.0 % of the weight, the crystallinity of polyolefine will become low and puncturing of the polyolefine fine porosity film will become difficult.

[0009] By adding polypropylene to polyethylene or its polyethylene constituent, microscopic irregularity arises on the front face of the obtained polyolefine fine porosity film. **1 micrometers or more of thickness fluctuation of less than 1mm of right-and-left four way types with which this microscopic irregularity adjoins each other in the direction of a field of a polyolefine film front face are **1 micrometer - **3 micrometers preferably. There is [thickness fluctuation] no effectiveness in improvement in the holdout of the electrolytic solution at less than **1 micrometer. the amount of the polypropylene used by this invention -- 5- of the whole polyolefine -- it is 5 - 25 % of the weight preferably 30% of the

weight. At less than 5 % of the weight, the irregularity distributed to homogeneity cannot be formed and the effectiveness on an electrolytic-solution maintenance disposition is not seen. [much] Moreover, if it exceeds 30 % of the weight, the reinforcement of the polyolefine fine porosity film will fall remarkably, if it increases further, polyethylene and polypropylene will carry out phase separation at the time of sheet forming, and shaping will become difficult.

[0010] The polyolefine fine porosity film of this invention mixes and carries out after [melting kneading] extrusion molding of an organic liquefied object or the solid-state to the resin constituent which added polypropylene to polyethylene or a polyethylene constituent, and is obtained by giving extract and extension. Moreover, even if it adds non-subtlety fine particles into the mixture of a resin constituent and an organic liquefied object, or a solid-state, it does not interfere at all. After supplying the good solvent of polyolefine to a polyolefine constituent, preparing the solution of a polyolefine constituent as a desirable method of obtaining the polyolefine fine porosity film of this invention and extruding this solution in the shape of a sheet from the die of an extruder, it is the approach of removing the solvent which cools, forms a gel constituent, carries out heating extension of this gel constituent, and remains after an appropriate time.

[0011] In this invention, the solution of the polyolefine constituent used as a raw material is prepared by carrying out the heating dissolution of the

above-mentioned polyolefine constituent at a solvent. As this solvent, especially if polyolefine can fully be dissolved, it will not be limited. For example, although the mineral oil fraction corresponding to these in the hydrocarbon of aliphatic series, such as a nonane, Deccan, an undecane, a dodecane, and a liquid paraffin, or a ring type or the boiling point etc. is raised, in order to obtain a gel moldings with a stable solvent content, the solvent of a non-volatile like a liquid paraffin is desirable. The heating dissolution is performed kneading with churning or an extruder powerfully at the temperature which polyolefine dissolves completely. The temperature has the desirable range of 140-250 degrees C. Moreover, the concentration of a polyolefine solution is 10 - 40 % of the weight preferably ten to 50% of the weight. At less than 10 % of the weight, in case the amount of solvents to be used fabricates about [not being mostly economical] and in the shape of a sheet, it becomes a swell and the neck in are large and difficult to fabricate concentration a sheet at a dice outlet. In addition, it is desirable to add an antioxidant, in order to prevent oxidation of polyolefine in the heating dissolution.

[0012] Next, the heating solution of this polyolefine constituent is preferably extruded and fabricated from a die. a die -- usually -- a rectangular mouthpiece -- although the sheet die which carried out the configuration is used, a double cylinder-like inflation die etc. can be used. The die gap at the time of using a

sheet die is usually 0.1-5mm, and extrusion-molding temperature is 140-250 degrees C. Under the present circumstances, an extrusion rate is usually a part for part [for 20-30cm/], and 10m/.

[0013] Thus, the solution extruded from the die is fabricated by the gel sheet by cooling. As for cooling, it is desirable to carry out the above rate by 50-degree-C/below to setting temperature at least. If a cooling rate is generally slow, the higher order structure of the gel sheet obtained will become coarse, and the false cell unit which forms it will also become big, but if a cooling rate is quick, it will become a dense cell unit. By 50-degree-C/, by the following, degree of crystallinity rises and a cooling rate cannot serve as a gel sheet suitable for extension easily. As the cooling approach, cold blast, cooling water, the method of making other cooling media contact directly, the method of making the roll cooled with the refrigerant contact, etc. can be used. in addition, the solution extruded from the die -- before cooling or under cooling -- desirable -- 1-10 -- you may take over by the taking over ratio of 1-5 more preferably. It comes [if a taking over ratio becomes ten or more, the neck in will become large, and / lifting-] to be easy of fracture at the time of extension and is not desirable.

[0014] Next, it extends to this gel moldings. Extension heats a gel sheet and the combination of the usual tenter method, the rolling method, a tubular film process, the rolling-out methods, or these approaches performs it for a

predetermined scale factor. Biaxial stretching is desirable although uniaxial stretching or biaxial stretching is sufficient as extension. Moreover, in the case of biaxial stretching, in-every-direction coincidence extension or any of serially extension is sufficient. Extension temperature is the range under of the crystal distribution temperature of polyolefine to a crystalline melting point preferably the melting point of +10 degrees C or less of polyolefine. Moreover, although draw magnification changes with thickness of an original fabric, in uniaxial stretching, more than twice are desirable and is three to 30 times more preferably. For a field scale factor, in biaxial stretching, 10 or more times is desirable, and they are 15 to 400 times more preferably. Less than 10 times of extension are [a field scale factor] insufficient, and high elasticity and the fine porosity film of high intensity are not obtained. On the other hand, if a field scale factor exceeds 400 times, constraint will arise in extension actuation etc.

[0015] The obtained extension moldings removes the solvent which washes and remains with a solvent. As a washing solvent, the thing of the easy-volatility of ether, such as hydrocarbons fluoride, such as 3 chlorinated-hydrocarbons [, such as hydrocarbons, such as a pentane, a hexane, and a heptane, a methylene chloride, and 4 salt carbon], ethane, etc. fluoride, diethylether, and dioxane, etc. can be used. these solvents are suitably chosen according to the solvent used for the dissolution of a polyolefine constituent, and are independent

-- or it mixes and uses. The washing approach can be performed by the approach which is immersed in a solvent and extracted, the approach of carrying out the shower of the solvent, or the approach by these combination.

[0016] The above washing is performed until the residual solvent in an extension moldings becomes less than 1% of the weight. Although a washing solvent is dried after that, the desiccation approach of a washing solvent can be performed by approaches, such as stoving and an air dried. As for the dry extension moldings, it is desirable to carry out heat setting in the temperature requirement of crystal distribution temperature - the melting point.

[0017] If the polyolefine fine porosity film manufactured as mentioned above has the small deflection when making it the Maki slit, and there are many amounts of maintenance of the electrolytic solution and it is used as a separator for cells, it can make the capacity high. In addition, the obtained polyolefine fine porosity film can perform surface qualification of hydrophilization processing of a plasma exposure, surfactant sinking in, a surface graft, etc. further if needed.

[0018]

[Example] Although an example is given to below about this invention and being further explained to a detail, especially this invention is not limited to an example. In addition, the test method in an example is as follows.

(1) Thickness : the cross section was measured with the scanning electron

microscope.

(2) Thickness fluctuation : thickness distribution of the polyolefine fine porosity film was measured continuously by the 0.1-micrometer high resolution by film SHIKKUNESU circuit tester KGby ANRITSU CORP.601A, and thickness distribution was measured.

(3) Breaking strength : it is ASTM about the breaking strength of a width-of-face a strip specimen of 15mm. It measured based on D882.

(4) Air permeability : JIS It measured based on P8117.

(5) Deflection : the deflection when beginning to roll 60mm width of face and the roll which carried out the slit to the 500m volume 1m was measured.

(6) The amount of electrolytic solutions : the amount of electrolytic solutions which pours in the electrolytic solution (propylene carbonate) from a side, and can be poured into the fine porosity film was measured, compressing a 10cmx10cm sample by the ten-sheet pile and the pressure of 5kg.

[0019] Example 1 weight average molecular weight obtained the polyolefine constituent with which 20 % of the weight (UHMWPE) of ultra high molecular weight polyethylene of 2.5x106, 60 % of the weight (HDPE) of high density polyethylene of 3.5x105, and weight average molecular weight added the antioxidant 0.375 weight section to the polyolefine constituent 100 weight section which the polypropylene of 5.1x105 becomes from 20 % of the weight.

This polyolefine constituent 30 weight section was supplied to the twin screw extruder (58mmphi, ratio-of-length-to-diameter=42, strong kneading type). Moreover, the liquid paraffin 70 weight section was supplied from the side feeder of this twin screw extruder, melting kneading was carried out by 200rpm, and the polyolefine solution was prepared in the extruder.

[0020] Then, it extruded at 190 degrees C from the T die installed at the tip of this extruder, and the gel sheet was fabricated while the cooling roller took over. Then, coincidence biaxial extension was performed for this gel sheet to 5x5 at 115 degrees C, and the extension film was obtained. After carrying out extract removal of the liquid paraffin which washes the obtained extension film with a methylene chloride, and remains, desiccation and heat treatment were performed and the polyolefine fine porosity film was obtained. The result of physical-properties evaluation of this polyolefine fine porosity film is shown in Table 1.

[0021] In example 2 example 1, the fine porosity film was obtained like the example 1 except having changed into the value which shows the amount of a resin constituent and the liquid paraffin used in Table 1. The result of physical-properties evaluation of the obtained polyolefine fine porosity film is shown in Table 1.

[0022] In example 3 example 1, the fine porosity film was obtained like the

example 1 except having changed into the value which shows the amount of the polypropylene used in Table 1. The result of physical-properties evaluation of the obtained polyolefine fine porosity film is shown in Table 1.

[0023] In example 4 example 1, the fine porosity film was obtained like the example 1 except having changed into the value which shows the molecular weight and the amount of the polypropylene used in Table 1. The result of physical-properties evaluation of the obtained polyolefine fine porosity film is shown in Table 1.

[0024] In example of comparison 1 example 1, the fine porosity film was obtained like the example 1 except not using polypropylene. The result of physical-properties evaluation of the obtained polyolefine fine porosity film is shown in Table 1.

[0025] Microscopic irregularity has arisen on the film front face, the polyolefine fine porosity film of this invention illustrated by examples 1-4 has little deflection at the time of shaping, and there are many amounts of electrolytic-solution maintenance so that clearly from Table 1. On the other hand, the polyethylene fine porosity film from the constituent which does not add polypropylene does not have microscopic irregularity in a film front face, the deflection at the time of shaping is large, and there are few amounts of electrolytic-solution maintenance (example 1 of a comparison).

[0026]

[Table 1]

	実　施　例				比較例
	1	2	3	4	1
ﾎﾟﾘｴﾁﾚﾝ UHMWPE(Mw)　(重量%) HDPE(Mw)　(重量%)	2.5×10^{6}(20) 3.5×10^{5}(60)	2.5×10^{6}(20) 3.5×10^{5}(70)	2.5×10^{6}(20) 3.5×10^{5}(70)	2.5×10^{6}(20) 3.5×10^{5}(60)	2.5×10^{6}(20) 3.3×10^{5}(60)
ﾎﾟﾘﾌﾟﾛﾋﾟﾚﾝ Mw　(重量%)	5.1×10^{5}(20)	5.1×10^{5}(10)	5.1×10^{5}(10)	1.5×10^{5}(20)	－
樹脂濃度(重量%)	30	40	30	30	30
流動ﾊﾟﾗﾌｨﾝ(重量%)	70	60	70	70	70
延伸条件 温度（℃） 倍率	115 5×5	115 5×5	115 5×5	115 5×5	115 5×5
膜物性 膜厚(μm) 厚み変動（μm） 破断強度 MD/TD（kg/cm^2） 透気度(秒/100cc) 曲がり（mm） 電解液量（g）	25.5 1.35 1100/950 550 1 0.95	26 1.10 1210/1010 690 1.5 0.73	26.8 1.20 1160/990 705 2.2 0.84	26.8 1.15 965/830 662 2.2 0.79	25 0.49 1250/1130 730 8 0.4

[0027]

[Effect of the Invention] Its deflection at the time of shaping can be small, and there are many amounts of electrolytic-solution maintenance, since the polyolefine fine porosity film of this invention is in high intensity and high permeability, its safety is high, and when using as a separator for high capacity lithium cells, it can greatly be trusted in respect of safety.

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(21)Application number : 10-090686 (71)Applicant : TONEN KAGAKU KK

(22)Date of filing : 20.03.1998 (72)Inventor : TAKITA KOTARO

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to cause microscopic recesses and projections on the surface of the polyolefin fine porous membrane and as a result, the moldability, the permeability and retention of an electrolyte are improved.

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[Claim 2] The separator for cells which consists of polyolefine fine porosity film according to claim 1.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

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[0002]

[Description of the Prior Art] The polyolefine fine porosity film is insoluble to an organic solvent, and to the electrolyte or the electrode active material, since it is stable, it is widely used as the separator of separator capacitors for large-sized cells, such as a separator of a cell especially a separator of the primary lithium ion and a rechargeable battery, and an electric vehicle, various kinds of demarcation membranes, the water treatment film, ultrafiltration membrane, a micro filter, or a base material of ****.

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the time of shaping etc., and the purpose of this invention is offering the polyolefine fine porosity film which was excellent in the amount of maintenance of the electrolytic solution while it is excellent in penetrable ability and a mechanical strength.

[0006]

[Means for Solving the Problem] this invention persons have improved the moldability and hit on an idea of the polyolefine fine porosity film which improved the permeability of the electrolytic solution and holdout being obtained to a header and this invention while they made the front face of the polyolefine fine porosity film produce microscopic irregularity and were excellent in penetrable ability and a mechanical strength by adding the polypropylene of the amount of specification to ultra high molecular weight polyethylene or its constituent, as a result of inquiring wholeheartedly, in order to attain the above-mentioned purpose. That is, this invention is polyolefine fine porosity film whose thickness fluctuation of less than 1mm of right-and-left four way types with which weight average molecular weight is the polyolefine fine porosity film which consists of 5x105 or more polyethylene or 70 - 95 % of the weight of a polyethylene constituent of those, and a polyolefine constituent with which weight average molecular weight contains 5 - 30 % of the weight of 1x104 or more polypropylene, and adjoins each other in the direction of a field on the front face of the film is **1

micrometers or more.

[0007]

[Embodiment of the Invention] The weight average molecular weight of the polyethylene used by this invention is polyethylene of the ultrahigh molecular weight of 1x106 to 15x106 preferably 5x105 or more. In the extension process at the time of manufacture of the fine porosity film, the maximum draw magnification has low weight average molecular weight at less than 5x105, and the target fine porosity film is not obtained. On the other hand, what exceeds 15x106 although especially an upper limit is not restrictive is inferior to a moldability in formation of the gel moldings at the time of manufacture of the fine porosity film. Moreover, in this invention, in order to aim at improvement in high-concentration-izing of the below-mentioned polyolefine solution, and the reinforcement of the fine porosity film, the constituent of with a weight average molecular weight of 1x106 or more ultra high molecular weight polyethylene, and 1x105 or more weight-average-molecular-weight less than 5x105 high density polyethylene can be used. The content in the polyethylene constituent of ultra high molecular weight polyethylene makes the whole polyethylene constituent 100 % of the weight, and 1 % of the weight or more is desirable, and it is 10 - 70 % of the weight more preferably. The weight average molecular weight/number average molecular weight furthermore used as a scale of the

molecular weight distribution of said polyethylene or its polyethylene constituent are 5-50 preferably 300 or less.

[0008] As polypropylene used by this invention, the gay polypropylene of 3.0x104 to 1.0x106 and an ethylene content can use [weight average molecular weight] 1.0 or less % of the weight of an ethylene propylene random copolymer, an ethylene propylene block copolymer, etc. preferably 1.0x104 or more. Puncturing of the polyolefine fine porosity film with which weight average molecular weight is obtained less than by 1.0x104 becomes difficult, if an ethylene content exceeds 1.0 % of the weight, the crystallinity of polyolefine will become low and puncturing of the polyolefine fine porosity film will become difficult.

[0009] By adding polypropylene to polyethylene or its polyethylene constituent, microscopic irregularity arises on the front face of the obtained polyolefine fine porosity film. **1 micrometers or more of thickness fluctuation of less than 1mm of right-and-left four way types with which this microscopic irregularity adjoins each other in the direction of a field of a polyolefine film front face are **1 micrometer - **3 micrometers preferably. There is [thickness fluctuation] no effectiveness in improvement in the holdout of the electrolytic solution at less than **1 micrometer. the amount of the polypropylene used by this invention -- 5- of the whole polyolefine -- it is 5 - 25 % of the weight preferably 30% of the

weight. At less than 5 % of the weight, the irregularity distributed to homogeneity cannot be formed and the effectiveness on an electrolytic-solution maintenance disposition is not seen. [much] Moreover, if it exceeds 30 % of the weight, the reinforcement of the polyolefine fine porosity film will fall remarkably, if it increases further, polyethylene and polypropylene will carry out phase separation at the time of sheet forming, and shaping will become difficult.

[0010] The polyolefine fine porosity film of this invention mixes and carries out after [melting kneading] extrusion molding of an organic liquefied object or the solid-state to the resin constituent which added polypropylene to polyethylene or a polyethylene constituent, and is obtained by giving extract and extension. Moreover, even if it adds non-subtlety fine particles into the mixture of a resin constituent and an organic liquefied object, or a solid-state, it does not interfere at all. After supplying the good solvent of polyolefine to a polyolefine constituent, preparing the solution of a polyolefine constituent as a desirable method of obtaining the polyolefine fine porosity film of this invention and extruding this solution in the shape of a sheet from the die of an extruder, it is the approach of removing the solvent which cools, forms a gel constituent, carries out heating extension of this gel constituent, and remains after an appropriate time.

[0011] In this invention, the solution of the polyolefine constituent used as a raw material is prepared by carrying out the heating dissolution of the

above-mentioned polyolefine constituent at a solvent. As this solvent, especially if polyolefine can fully be dissolved, it will not be limited. For example, although the mineral oil fraction corresponding to these in the hydrocarbon of aliphatic series, such as a nonane, Deccan, an undecane, a dodecane, and a liquid paraffin, or a ring type or the boiling point etc. is raised, in order to obtain a gel moldings with a stable solvent content, the solvent of a non-volatile like a liquid paraffin is desirable. The heating dissolution is performed kneading with churning or an extruder powerfully at the temperature which polyolefine dissolves completely. The temperature has the desirable range of 140-250 degrees C. Moreover, the concentration of a polyolefine solution is 10 - 40 % of the weight preferably ten to 50% of the weight. At less than 10 % of the weight, in case the amount of solvents to be used fabricates about [not being mostly economical] and in the shape of a sheet, it becomes a swell and the neck in are large and difficult to fabricate concentration a sheet at a dice outlet. In addition, it is desirable to add an antioxidant, in order to prevent oxidation of polyolefine in the heating dissolution.

[0012] Next, the heating solution of this polyolefine constituent is preferably extruded and fabricated from a die. a die -- usually -- a rectangular mouthpiece -- although the sheet die which carried out the configuration is used, a double cylinder-like inflation die etc. can be used. The die gap at the time of using a

sheet die is usually 0.1-5mm, and extrusion-molding temperature is 140-250 degrees C. Under the present circumstances, an extrusion rate is usually a part for part [for 20-30cm/], and 10m/.

[0013] Thus, the solution extruded from the die is fabricated by the gel sheet by cooling. As for cooling, it is desirable to carry out the above rate by 50-degree-C/below to setting temperature at least. If a cooling rate is generally slow, the higher order structure of the gel sheet obtained will become coarse, and the false cell unit which forms it will also become big, but if a cooling rate is quick, it will become a dense cell unit. By 50-degree-C/, by the following, degree of crystallinity rises and a cooling rate cannot serve as a gel sheet suitable for extension easily. As the cooling approach, cold blast, cooling water, the method of making other cooling media contact directly, the method of making the roll cooled with the refrigerant contact, etc. can be used. in addition, the solution extruded from the die -- before cooling or under cooling -- desirable -- 1-10 -- you may take over by the taking over ratio of 1-5 more preferably. It comes [if a taking over ratio becomes ten or more, the neck in will become large, and / lifting-] to be easy of fracture at the time of extension and is not desirable.

[0014] Next, it extends to this gel moldings. Extension heats a gel sheet and the combination of the usual tenter method, the rolling method, a tubular film process, the rolling-out methods, or these approaches performs it for a

predetermined scale factor. Biaxial stretching is desirable although uniaxial stretching or biaxial stretching is sufficient as extension. Moreover, in the case of biaxial stretching, in-every-direction coincidence extension or any of serially extension is sufficient. Extension temperature is the range under of the crystal distribution temperature of polyolefine to a crystalline melting point preferably the melting point of +10 degrees C or less of polyolefine. Moreover, although draw magnification changes with thickness of an original fabric, in uniaxial stretching, more than twice are desirable and is three to 30 times more preferably. For a field scale factor, in biaxial stretching, 10 or more times is desirable, and they are 15 to 400 times more preferably. Less than 10 times of extension are [a field scale factor] insufficient, and high elasticity and the fine porosity film of high intensity are not obtained. On the other hand, if a field scale factor exceeds 400 times, constraint will arise in extension actuation etc.

[0015] The obtained extension moldings removes the solvent which washes and remains with a solvent. As a washing solvent, the thing of the easy-volatility of ether, such as hydrocarbons fluoride, such as 3 chlorinated-hydrocarbons [, such as hydrocarbons, such as a pentane, a hexane, and a heptane, a methylene chloride, and 4 salt carbon], ethane, etc. fluoride, diethylether, and dioxane, etc. can be used. these solvents are suitably chosen according to the solvent used for the dissolution of a polyolefine constituent, and are independent

-- or it mixes and uses. The washing approach can be performed by the approach which is immersed in a solvent and extracted, the approach of carrying out the shower of the solvent, or the approach by these combination.

[0016] The above washing is performed until the residual solvent in an extension moldings becomes less than 1% of the weight. Although a washing solvent is dried after that, the desiccation approach of a washing solvent can be performed by approaches, such as stoving and an air dried. As for the dry extension moldings, it is desirable to carry out heat setting in the temperature requirement of crystal distribution temperature - the melting point.

[0017] If the polyolefine fine porosity film manufactured as mentioned above has the small deflection when making it the Maki slit, and there are many amounts of maintenance of the electrolytic solution and it is used as a separator for cells, it can make the capacity high. In addition, the obtained polyolefine fine porosity film can perform surface qualification of hydrophilization processing of a plasma exposure, surfactant sinking in, a surface graft, etc. further if needed.

[0018]

[Example] Although an example is given to below about this invention and being further explained to a detail, especially this invention is not limited to an example. In addition, the test method in an example is as follows.

(1) Thickness : the cross section was measured with the scanning electron

microscope.

(2) Thickness fluctuation : thickness distribution of the polyolefine fine porosity film was measured continuously by the 0.1-micrometer high resolution by film SHIKKUNESU circuit tester KGby ANRITSU CORP.601A, and thickness distribution was measured.

(3) Breaking strength : it is ASTM about the breaking strength of a width-of-face a strip specimen of 15mm. It measured based on D882.

(4) Air permeability : JIS It measured based on P8117.

(5) Deflection : the deflection when beginning to roll 60mm width of face and the roll which carried out the slit to the 500m volume 1m was measured.

(6) The amount of electrolytic solutions : the amount of electrolytic solutions which pours in the electrolytic solution (propylene carbonate) from a side, and can be poured into the fine porosity film was measured, compressing a 10cmx10cm sample by the ten-sheet pile and the pressure of 5kg.

[0019] Example 1 weight average molecular weight obtained the polyolefine constituent with which 20 % of the weight (UHMWPE) of ultra high molecular weight polyethylene of 2.5x106, 60 % of the weight (HDPE) of high density polyethylene of 3.5x105, and weight average molecular weight added the antioxidant 0.375 weight section to the polyolefine constituent 100 weight section which the polypropylene of 5.1x105 becomes from 20 % of the weight.

This polyolefine constituent 30 weight section was supplied to the twin screw extruder (58mmphi, ratio-of-length-to-diameter=42, strong kneading type). Moreover, the liquid paraffin 70 weight section was supplied from the side feeder of this twin screw extruder, melting kneading was carried out by 200rpm, and the polyolefine solution was prepared in the extruder.

[0020] Then, it extruded at 190 degrees C from the T die installed at the tip of this extruder, and the gel sheet was fabricated while the cooling roller took over. Then, coincidence biaxial extension was performed for this gel sheet to 5x5 at 115 degrees C, and the extension film was obtained. After carrying out extract removal of the liquid paraffin which washes the obtained extension film with a methylene chloride, and remains, desiccation and heat treatment were performed and the polyolefine fine porosity film was obtained. The result of physical-properties evaluation of this polyolefine fine porosity film is shown in Table 1.

[0021] In example 2 example 1, the fine porosity film was obtained like the example 1 except having changed into the value which shows the amount of a resin constituent and the liquid paraffin used in Table 1. The result of physical-properties evaluation of the obtained polyolefine fine porosity film is shown in Table 1.

[0022] In example 3 example 1, the fine porosity film was obtained like the

example 1 except having changed into the value which shows the amount of the polypropylene used in Table 1. The result of physical-properties evaluation of the obtained polyolefine fine porosity film is shown in Table 1.

[0023] In example 4 example 1, the fine porosity film was obtained like the example 1 except having changed into the value which shows the molecular weight and the amount of the polypropylene used in Table 1. The result of physical-properties evaluation of the obtained polyolefine fine porosity film is shown in Table 1.

[0024] In example of comparison 1 example 1, the fine porosity film was obtained like the example 1 except not using polypropylene. The result of physical-properties evaluation of the obtained polyolefine fine porosity film is shown in Table 1.

[0025] Microscopic irregularity has arisen on the film front face, the polyolefine fine porosity film of this invention illustrated by examples 1-4 has little deflection at the time of shaping, and there are many amounts of electrolytic-solution maintenance so that clearly from Table 1. On the other hand, the polyethylene fine porosity film from the constituent which does not add polypropylene does not have microscopic irregularity in a film front face, the deflection at the time of shaping is large, and there are few amounts of electrolytic-solution maintenance (example 1 of a comparison).

[0026]

[Table 1]

	実施例				比較例
	1	2	3	4	1
ﾎﾟﾘｴﾁﾚﾝ UHMWPE(Mw) (重量%) HDPE(Mw) (重量%)	2.5×10^6(20) 3.5×10^5(60)	2.5×10^6(20) 3.5×10^5(70)	2.5×10^6(20) 3.5×10^5(70)	2.5×10^6(20) 3.5×10^5(60)	2.5×10^6(20) 3.3×10^5(60)
ﾎﾟﾘﾌﾟﾛﾋﾟﾚﾝ Mw (重量%)	5.1×10^5(20)	5.1×10^5(10)	5.1×10^5(10)	1.5×10^5(20)	–
樹脂濃度(重量%)	30	40	30	30	30
流動ﾊﾟﾗﾌｨﾝ(重量%)	70	60	70	70	70
延伸条件 温度 (℃) 倍率	 115 5×5	 115 5×5	 115 5×5	 115 5×5	 115 5×5
膜物性 膜厚(μm) 厚み変動 (μm) 破断強度 MD/TD (kg/cm^2) 透気度(秒/100cc) 曲がり (mm) 電解液量 (g)	 25.5 1.35 1100/950 550 1 0.95	 26 1.10 1210/1010 690 1.5 0.73	 26.8 1.20 1160/990 705 2.2 0.84	 26.8 1.15 965/830 662 2.2 0.79	 25 0.49 1250/1130 730 8 0.4

[0027]

[Effect of the Invention] Its deflection at the time of shaping can be small, and there are many amounts of electrolytic-solution maintenance, since the polyolefine fine porosity film of this invention is in high intensity and high permeability, its safety is high, and when using as a separator for high capacity lithium cells, it can greatly be trusted in respect of safety.